Electronic Supporting Information

Experimental

Materials

Hexane (Fisher, HPLC grade), dioxane (Aldrich, sure-seal), dimethylsulfoxide (Aldrich, sure-seal) 1-phenyl-1-(trimethylsiloxy)ethylene, **1**, (Aldrich, 98%), 4-(Dimethylamino)pyridine (Aldrich, 99%), N,N'-ethylenebis(acryl amide) (EBAAm) (Aldrich, technical grade) and 4,4'-Azobis(4-cyanovaleric acid) (ACVA) (Aldich, purum, ≥98.0%) were used as purchased. Benzoyl peroxide (Aldrich, 70% in H_2O) was recrystallised from $CHCl_3$ (Fisher, reagent grade) and MeOH (Fisher, HPLC grade). NIPAM (Aldrich, 97%) was recrystallised (x3) from hexane via dissolution at 45°C and then cooled under refrigeration. Methyl methacrylate (Aldrich, 99%) and styrene (Aldrich, 99%) were distilled before use. α-Cyano-4-hydroxycinnamic acid (Fluka, puriss. p.a. ≥99.0%), dithranol (Aldrich, 97%), sodium trifluoroacetate (Fluka, puriss. p.a. ≥99.0%) and silver trifluoroacetate (Aldrich, 99.0%) were used as purchased.

Synthesis of linear PNIPAM initiated with ACVA

The following general procedure was used: NIPAM (500-1000 mg) was dissolved in dioxane (5-10 ml) and **1** (8.5-339.6 mg) was added followed by ACVA (6.9-123.9 mg). This mixture was stirred at room temperature for 10 min until all of the starting materials had dissolved and then transferred to a 20 ml ampoule. The solution was subjected to 4x freeze-pump-thaw cycles to a pressure of 10^{-4} mbar. The ampoule was then flame sealed and heated to 60°C for 24 or 48 hours in a thermostated water bath. The polymer solutions were then precipitated into diethyl ether (250 ml), the ether was decanted off and the procedure repeated. The polymer was then dried in vacuo at room temperature for 24h to give white solids.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ7.90, (2H, br, Ar), δ7.55, (1H, br, Ar), δ7.45, (2H, br, Ar), δ7.10-6.50, (1H, br, N**H**), δ4.00, (1H, br, NHC**H**$(CH_3)_3$), δ2.20, (1H, br, C**H**CO), δ1.65, (d, 2H, CHC**H$_2$**), δ1.10, (d, 6H, CH(C**H$_3$**)$_2$), δ0.20, (s, 18H, $Si_2(CH_3)_6$).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ175 (1C, **C**O), δ145 (1C, Ar), δ129 (4C, Ar), δ127 (1C, Ar), δ43 (1C, CH_2**C**H), δ41 (NIPAM, 1C, **C**H_2CH), δ22, (2C, (**C**H_3)$_2$).

The polymerizations were repeated in the absence of **1**.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ7.10-6.50, (1H, br, N**H**), δ4.00 (1H, br, NHC**H**$(CH_3)_3$), δ2.20 (1H, br, C**H**CO), δ1.65 (2H, br, CHC**H$_2$**), δ1.10 (6H, br, CH(C**H$_3$**)$_2$).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ175 (1C, **C**O), δ43 (1C, CH_2**C**H), δ41 (NIPAM, 1C, **C**H_2CH), δ22, (2C, (**C**H_3)$_2$).

Synthesis of linear PMMA initiated with ACVA

Synthesised as above, but using the following: Methyl methacrylate (500 mg, 4.994 mmol), ACVA (23.3 mg-139.0 mg), **1** (32-96 mg) and dioxane (5ml). The polymers were precipitated into petroleum ether 40/60.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ8.15-7.80, (2H, br, Ar), δ7.65-7.35, (1H, br, Ar), δ3.65, (3H, br, OC**H$_3$**), δ1.00 (2H, br, CC**H$_2$**), δ0.80 (3H, br, CC**H$_3$**), δ0.15 (18H, br, $Si_2(C\mathbf{H_3})_6$.

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ178, δ177 (1C, **C**O), δ145 (1C, Ar), δ129 (4C, Ar), δ127 (1C, Ar), δ54, δ51 (1C, O**C**H_3), δ44 (1C, α-**C**CH_3), δ18, δ16 (1C, (C**C**H_3) (duplicate signals due to different PMMA tacticities).

The polymerizations were repeated in the absence of **1**.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ3.65, (3H, br, OC**H$_3$**), δ1.00 (2H, br, CC**H$_2$**), δ0.80 (3H, br, CC**H$_3$**).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ178, δ177 (1C, **C**O), δ54, δ51 (1C, O**C**H_3), δ44 (1C, α-**C**CH_3), δ18, δ16 (1C, (C**C**H_3) (duplicate signals due to different PMMA tacticities).

Synthesis of linear polystyrene samples initiated with ACVA

Synthesised as above, but using the following: Styrene (500 mg, 4.40 mmol), ACVA (20.6 mg-62.0mg), **1** (28.2-84.5 mg) and dioxane (5 ml).

^{1}H NMR: (250MHz, $CDCl_3$): (ppm) δ7.25-6.80, (2H, br, Ar), δ6.75-6.30, (1H, br, Ar), δ1.85, (1H, br, CH_2C**H)**, δ1.40 (2H, br, CHC**H$_2$**), δ0.15 (18H, br, $Si_2(C\mathbf{H_3})_6$.

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ145 (1C, **C**, Ar), δ128 (4C, **C**, Ar), δ125 (1C, Ar), δ54, δ45 (1C, **C**H_2CH), δ40 (1C, **C**CH_2).

The polymerizations were repeated in the absence of **1**.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ7.15, (2H, br, Ar), δ6.60, (1H, br, Ar), δ1.85, (1H, br, CH_2C**H)**, δ1.40 (2H, br, CHC**H$_2$**).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ145 (1C, **C**, Ar), δ128 (4C, **C**, Ar), δ125 (1C, Ar), δ54, δ45 (1C, **C**H_2CH), δ40 (1C, **C**CH_2).

Synthesis of linear PNIPAM with redox initiator system: BPO/DMAP

NIPAM (1000 mg, 8.84 mmol), **1** (37-133 mg), BPO (48-143 mg, 0.589 mmol) and DMAP (24-72 mg, 0.589 mmol) were dissolved in dioxane (10 ml) at room temperature in a sealed flask under N_2. This mixture was stirred for 10 min until all of the starting materials had dissolved. The solution was transferred to a 20 ml glass ampoule. The solution was subjected to 4x freeze-pump-thaw cycles to a pressure of 10^{-4} mbar. The ampoule was then flame sealed and heated to 30^{o}C for 24 hours in a thermostated water bath. The polymer solutions

were then precipitated into diethyl ether (250 ml), the ether was decanted off and the procedure repeated. The polymer was then dried in vacuo at room temperature for 24h to give white solids.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ8.12, (2H, br, Ar), δ7.85, (2H, br, Ar), δ7.50, (2H, br, Ar), δ7.40, (5H, br, Ar), δ7.35-6.00, (1H, br, N**H**), δ4.00 (1H, br, NHC**H**$(CH_3)_3$), δ2.20 (1H, br, C**H**CO), δ1.65 (2H, br, CHC**H$_2$**), δ1.10 (6H, br, CH(C**H$_3$**)$_2$).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ175 (1C, **C**O), δ153 (BPO, 1C, Ar), δ145 (1C, Ar), δ133 (4C, Ar), δ131 (1C, Ar), δ129 (4C, Ar), δ127 (1C, Ar), δ43 (1C, CH_2**C**H), δ41 (NIPAM, 1C, **C**H_2CH), δ22, (2C, (**C**H_3)$_2$).

The polymerizations were repeated in the absence of **1**.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ8.15, (2H, br, Ar), δ7.40, (3H, br, Ar), δ7.10-6.50, (1H, br, N**H**), δ4.00 (1H, br, NHC**H**$(CH_3)_3$), δ2.20 (1H, br, C**H**CO), δ1.65 (2H, br, CHC**H$_2$**), δ1.10 (6H, br, CH(C**H$_3$**)$_2$).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ175 (1C, **C**O), δ153 (BPO, 1C, Ar), δ133 (BPO, 4C, Ar), δ131 (BPO, 1C, Ar), δ43 (1C, CH_2**C**H), δ41 (NIPAM, 1C, **C**H_2CH), δ22, (2C, (**C**H_3)$_2$).

Synthesis of linear PS with redox initiator system: BPO/DMAP

Synthesised as above, but using the following quantities: Styrene (1000 mg), 1-phenyl-1-(trimethylsiloxy)ethylene (41-123 mg), benzoyl peroxide (52-155 mgl), 4-dimethylamino pyridine (26-78 mg) and dioxane (10 ml).

^{1}H NMR: (250MHz, $CDCl_3$): (ppm) δ8.15, (2H, br, Ar), δ7.90, (2H, br, Ar), δ7.45, (2H, br, Ar), δ7.40, (5H, br, Ar), δ7.10, (2H, br, Ar), δ6.60, (2H, br, Ar), δ6.50, (1H, br, Ar), δ1.85 (1H, br, CH_2C**H**), δ1.45, (2H, br, CHC**H$_2$**).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ153 (BPO, 1C, Ar), δ145 (1C, **C**, Ar), δ133 (BPO, 4C, Ar), δ131 (BPO, 1C, Ar), δ128 (4C, **C**, Ar), δ125 (1C, Ar), δ54, δ45 (1C, **C**H_2CH), δ40 (1C, **C**CH_2).

The polymerizations were repeated in the absence of **1**.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ8.15, (2H, br, Ar), δ7.40, (3H, br, Ar), δ7.10, (2H, br, Ar), δ6.60, (2H, br, Ar), δ6.50, (1H, br, Ar), δ1.85, (1H, br, CH_2C**H**), δ1.40 (2H, br, CHC**H$_2$**).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ153 (BPO, 1C, Ar), δ145 (1C, **C**, Ar), δ133 (BPO, 4C, Ar), δ131 (BPO, 1C, Ar), δ128 (4C, **C**, Ar), δ125 (1C, Ar), δ54, δ45 (1C, **C**H_2CH), δ40 (1C, **C**CH_2).

Synthesis of linear PMMA with redox initiator system: BPO/DMAP

Synthesised as above, but using the following quantities: Styrene (1000 mg), 1-phenyl-1-(trimethylsiloxy)ethylene (41-123 mg), benzoyl peroxide (52-155 mgl), 4-dimethylamino pyridine (26-78 mg) and dioxane (10 ml).

^{1}H NMR: (250MHz, $CDCl_3$): (ppm) δ8.15, (2H, br, Ar), δ7.90, (2H, br, Ar), δ7.45, (2H, br, Ar), δ7.40, (5H, br, Ar), δ3.65, (br, 3H, OC**H$_3$**), δ1.00 (2H, br, CC**H$_2$**), δ0.80 (3H, br, CC**H$_3$**), δ0.15 (18H, br, $Si_2(C\mathbf{H_3})_6$.

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ178, δ177 (1C, **C**O), δ153 (BPO, 1C, Ar), δ145 (1C, Ar), δ133 (BPO, 4C, Ar), δ131 (BPO, 1C, Ar), δ129 (4C, Ar), δ127 (1C, Ar), δ54, δ51 (1C, O**C**H_3), δ44 (1C, α-**C**CH_3), δ18, δ16 (1C, (C**C**H_3) (duplicate signals due to different PMMA tacticities).

The polymerizations were repeated in the absence of **1**.

^{1}H NMR: (400MHz, $CDCl_3$): (ppm) δ8.15, (2H, br, Ar), δ7.45, (3H, br, Ar) δ3.65, (3H, br, OC**H$_3$**), δ1.00 (2H, br, CC**H$_2$**), δ0.80 (3H, br, CC**H$_3$**).

^{13}C NMR: (400MHz, $CDCl_3$) (ppm): δ178, δ177 (1C, **C**O), δ153 (BPO, 1C, Ar), δ133 (BPO, 4C, Ar), δ131 (BPO, 1C, Ar), δ54, δ51 (1C, O**C**H_3), δ44 (1C, α-**C**CH_3), δ18, δ16 (1C, (C**C**H_3) (duplicate signals due to different PMMA tacticities).

Synthesis of highly branched P(NIPAM)-co-(EBAAm)

NIPAM (500 mg, 4.42 mmol), EBAAm (74 mg, 0.443 mmol), **1** (172 mg, 0.886 mmol) and DMAP (54 mg, 0.886 mmol) were added to a 25 ml, 1 neck round bottomed flask fitted with a stirrer bar and a suba seal. Anhydrous DMSO (5 ml) was added to the flask and the mixture was stirred until all the reagents were dissolved. The flask was heated to 30^{o}C and purged with nitrogen for 20 minutes. BPO (107 mg, 0.886 mmol) was dissolved in 2 ml of anhydrous DMSO in a sample tube and was then injected into the reaction mixture. The reaction mixture was stirred for 1 hour before methanol (5 ml) was added to the flask and the solution was precipitated into diethyl ether (250 ml). The polymer was further washed with ether (2x100 ml) and allowed to dry in vacuo at room temperature for 16 hours. The polymer was redissolved in methanol (15 ml) and the procedure was repeated twice. The polymer was finally dried in vacuo at room temperature to give 138 mg (24%) of a white solid.

^{1}H NMR: (400MHz, MeOD): (ppm) δ8.25, (2H, br, Ar), δ7.65, (2H, br, Ar), δ7.50, (br, Ar), δ7.40, (4H, br, Ar), δ6.65, (4H, br, NH-$(C\mathbf{H_2})_2$-NH), (1H, br, CH_2=C**H**), δ6.25, δ5.70, (2H. br, C**H$_2$**=CH), δ3.75, (1H, br, NHC**H**), δ2.90, (br, 1H, NHC**H**$(CH_3)_3$), δ1.90 (t, 1H, C**H**CO), δ1.45 (d, 2H, CHC**H$_2$**), δ1.00 (d, 6H, $CH(C\mathbf{H_3})_2$)

^{13}C NMR: (500MHz, MeOD) (ppm): δ175 (EBAAm, 1C, **C**=O), δ173 (NIPAM, 1C, **C**=O), δ138 (Initiator, 1C, Ar), δ128 (SEE, 1C, Ar), δ126-129 (10C, Ar), δ116 (EBAAm, 1C, **C**H=CH_2), δ115 (EBAAm, 1C, CH=**C**H_2), δ44 (EBAAm, 1C, **C**H_2NH (mono-reacted)),

δ42(EBAAm, 1C, **C**H_2NH (fully-reacted)), δ41 (NIPAM, 1C, CH_2**C**H), δ40 (NIPAM, 1C, **C**H_2CH), δ21 (NIPAM, 2C, (**C**H_3)$_2$).

Synthesis of highly branched P(NIPAM-co-EBAAm) using continuous feed of 1 or 1 with BPO/DMAP

NIPAM (2000 mg, 17.68 mmol), EBAAm (296 mg, 1.77 mmol), **1** (172 mg, 0.88 mmol), and (1) BPO (429 mg, 1.77 mmol) or (2) BPO (107 mg, 0.44 mmol) and DMAP (1) (216 mg, 1.77 mmol) or (2) DMAP (54 mg, 0.44 mmol) were added to a 2 neck round bottomed flask fitted with a stirrer bar and 2 suba seals. Anhydrous DMSO (18 ml) was added to the flask and the mixture was stirred until all the reagents were dissolved. The flask was heated to 30^{o}C and purged with nitrogen for 20 minutes. Benzoyl peroxide (428 mg, 1.77 mmol) was dissolved in 2 ml of anhydrous DMSO in a sample tube and was then injected into the reaction mixture. Using a syringe pump either: (1) **1** (516 mg, 2.64 mmol) or (2) **1** (516 mg, 2.64 mmol) dissolved in DMSO and (2) BPO (322 mg, 1.33 mmol) and DMAP (162 mg, 1.33) also dissolved in DMSO (7 ml) was added over a period of 7 hours (using separate syringe pumps for BPO/DMAP and **1**). Once the feed had finished, methanol (10 ml) was added to the flask before the polymer was precipitated into diethyl ether (600 ml). The polymer was further washed with ether (2 x 100 ml) and allowed to dry in vacuo at room temperature for 16 hours. The polymer was redissolved in methanol (15 ml) and the procedure was repeated twice. The polymer was finally dried in vacuo at room temperature to give (1) 1.65 g (72%) and (2) 1.95 g (85%) of white solids.

^{1}H NMR: (400MHz, MeOD) (ppm): δ8.25, (2H, br, Ar), δ7.65, (2H, br, Ar), δ7.50, (br, Ar), δ7.40, (4H, br, Ar), δ6.65, (4H, br, NH-(C**H$_2$**)$_2$-NH), (1H, br, CH_2=C**H**), δ6.25, δ5.70, (2H. br, C**H$_2$**=CH), δ3.75, (1H, br, NHC**H**), δ2.90, (br, 1H, NHC**H**(CH_3)$_3$), δ1.90 (t, 1H, C**H**CO), δ1.45 (d, 2H, CHC**H$_2$**), δ1.00 (d, 6H, CH(C**H$_3$**)$_2$)

^{13}C NMR: (500MHz, MeOD) (ppm): δ175 (EBAAm, 1C, **C**=O), δ173 (NIPAM, 1C, **C**=O), δ138 (Initiator, 1C, Ar), δ128 (SEE, 1C, Ar), δ126-129 (10C, Ar), δ116 (EBAAm, 1C, **C**H=CH_2), δ115 (EBAAm, 1C, CH=**C**H_2), δ44 (EBAAm, 1C, **C**H_2NH (mono-reacted)), δ42(EBAAm, 1C, **C**H_2NH (fully-reacted)), δ41 (NIPAM, 1C, CH_2**C**H), δ40 (NIPAM, 1C, **C**H_2CH), δ21 (NIPAM, 2C, (**C**H_3)$_2$).

Cloud point determination

Turbidimetry measurements of aqueous solutions of polymers were performed using a Varian Cary 3 Bio UV-vis spectrometer. The temperature of the cell holder was controlled with a Varian Cary temperature controller to an accuracy of ±0.1^{o}C. Deionised water was obtained from a Millipore (Milli-Q) purification system at a resistivity of 18.2 Ω.cm^{-1}. Sample concentration was 1 mg/ml and the heating rate was 1^{o}C min^{-1}.

Matrix-Assisted Laser-Desorption-Ionisation Time of Flight Mass Spectra (MALDI-ToF MS)

MALDI-ToF-MS were obtained with a Micromass ToF Spec 2E spectrometer. The instrument was operated in positive ion reflectron mode with an accelerating potential of 20 kV. The instrument was calibrated using angiotensin II (1046.54 g mol^{-1}) and insulin (5734.61 g mol^{-1}).

Sample Preparation

Samples of PNIPAM, PMMA and sodium trifluoroacetate were made up (10 mg/ml^{-1}) in THF (HPLC grade) and α-Cyano-4-hydroxycinnamic acid was made up at a concentration of 20 mg/ml^{-1} also in THF. The spotting mixture consisted of a volume ratio of 10:1:1 matrix: polymer: salt. 1µl volumes of the mixture were applied to the plate. PS was also made up at 10 mg/ml^{-1} in THF but dithranol (20 mg/ml^{-1} in THF) was used as the matrix with silver trifluoroacetate (10 mg/ml^{-1}) as the salt. The spotting mixture consisted of a 20:1:1 volume ratio of matrix: polymer: salt.

^{1}H NMR & ^{13}C NMR

NMR spectra were recorded on either a Bruker AC-250, AMX2-400 or DRX-500 instrument at ambient temperature in either deuterated chloroform (Linear PNIPAM, PMMA, PS) or deuterated methanol (P(NIPAM)-co-(EBAAm).

Size Exclusion Chromatography (SEC)

Linear PNIPAM and PMMA Samples

Average molecular weight and molecular weight distributions (measured relative to poly(ethylene oxide) (PEO) or poly(MMA) standards) of polymers were measured by SEC with PL gel mixed-B (10 µm particle size, 100-10^6 Å pore size, effective MW range 10^3-10^6, 3x30 cm + guard columns) (Polymer Laboratories, UK) with a RI detector. *N,N*-dimethylformamide (DMF) containing 0.1 weight % lithium bromide was used as the eluent at a flow rate of 1.0 ml/min^{-1} at 70^{o}C. Sample concentrations were approximately 2.0 mg/ml^{-3} and were filtered prior to injection. Samples were injected through a Rheodyne 7725i injection port with a 200 µl loop.

Linear PS Samples

PS molecular weight distributions (measured relative to PS standards) were measured using a PL gel mixed-B (10 µm particle size, 100-10^6 Å pore size, effective MW range 10^3-10^6, 3x30 cm + guard columns) (Polymer Laboratories, UK) with an Erma ERC-7512 R.I. Detector. The mobile phase was THF (GPC grade) set at a flow rate of 1 ml/min^{-1}. Sample concentrations were approximately 2.0 mg/ml^{-1} and were filtered before injection. Samples were injected using a Gilson 234 auto injector.

Branched P(NIPAM)-co(EBAAm) Samples

Analysis were conducted by Viscotek™ (a Malvern company) on a DMF triple detection instrument using 3 ViscoGEL I-MBMMW columns and a TDA305 detector. The mobile phase was DMF containing 0.1M LiBr at a flow rate of 1 ml/min at 60°C. The samples were filtered before injection through a 100 µl loop. The detector was calibrated using a broad and a narrow PMMA standard.

Supporting results

ESI Figures and tables

A) PNIPAM produced in presence of **1** at 60˚C (ACVA)

Molar Feed Ratio of NIPAM/ACVA/SEE	Conc. / mmol/dm^{-3}			Conv. %	Mn	Mw	PD
	NIPAM	ACVA	SEE				
10/1/1[a]	912.9	91.3	91.3	24	1400	2500	1.8
20/1/1[a]	912.9	45.6	45.6	43	2800	5300	1.9
30/1/1[a]	912.9	30.4	30.4	52	3000	6300	2.1
50/1/1[a]	912.9	18.3	18.3	65	3800	8300	2.2
100/1/1[a]	912.9	9.1	9.1	67	5200	12100	2.3
30/1 (No SEE)[a]	912.9	30.4	-	83	26000	69700	2.7
30/1/2[a]	912.9	30.4	60.9	25	7200	15000	2.1
30/1/4[a]	912.9	30.4	121.7	16	7400	14800	2.0
30/1/6[a]	912.9	30.4	365.2	10	7700	14600	1.9
30/1/2[b]	912.9	30.4	121.7	26	7700	14600	1.9
30/1/6[b]	912.9	30.4	365.2	24	6600	13200	2.0

Table ESI 1. Feed ratios of NIPAM, ACVA and **1** and the respective molecular weights and conversions obtained. Polymerisation time of 24hrs[b], 48hrs[c]

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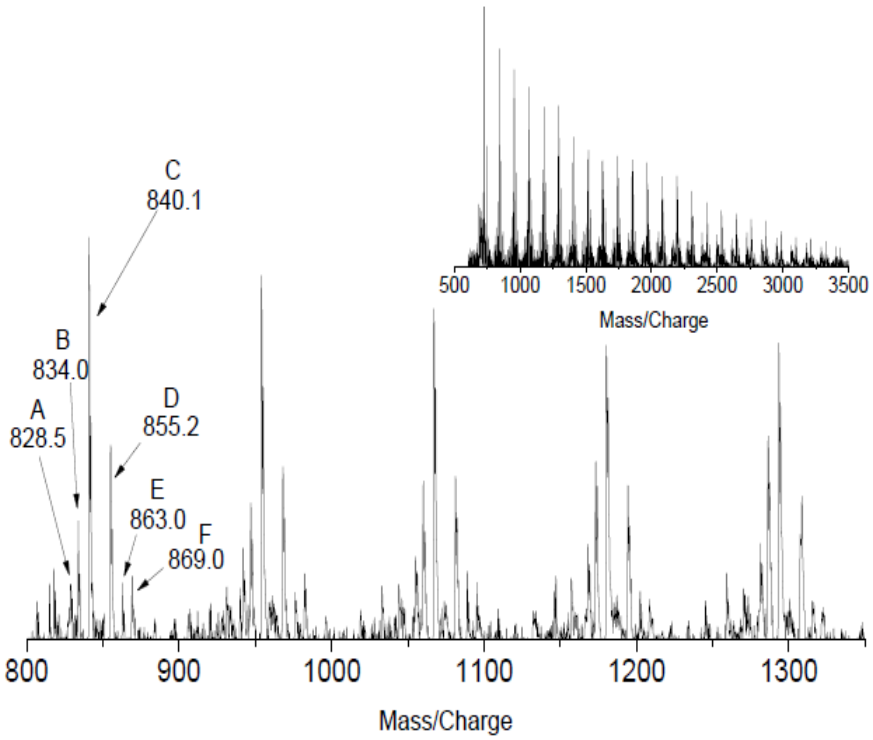


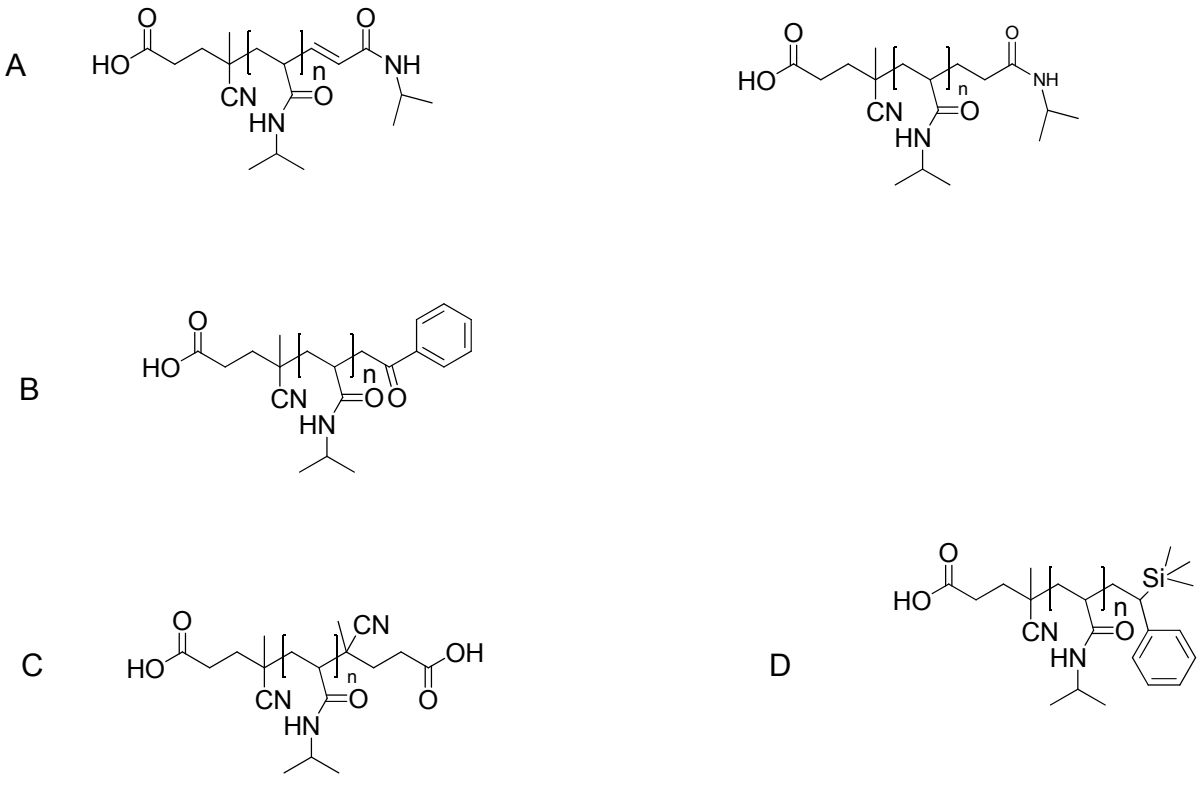


Fig. ESI 1 MALDI ToF mass spectrum of PNIPAM prepared in the presence of **1** and the various end group structures observed**.**

B) PS produced in presence of **1** at 60˚C (ACVA)

Molar Feed Ratio of Styrene/ACVA/SEE	Conc. / mmol/dm^{-3}			Conv. %	Mn	Mw	PD
	Styrene	ACVA	SEE				
10/1/1	991.2	99.1	99.1	6	3700	4800	1.3
20/1/1	991.2	49.6	49.6	25	3900	5900	1.5
30/1/1	991.2	33.0	33.0	27	4700	7200	1.5
30/1 (No SEE)	991.2	33.0	-	34	5300	9700	1.8

Table ESI 3 Feed ratios of styrene, ACVA and SEE (**1**) and the respective molecular weights and conversions obtained.

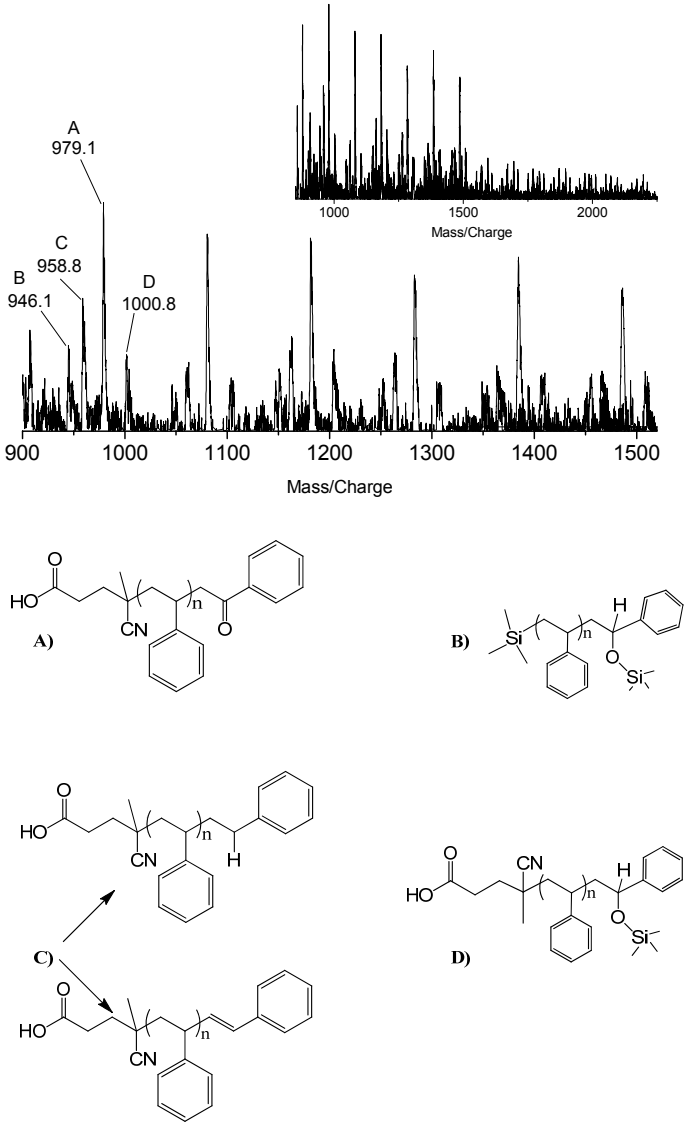
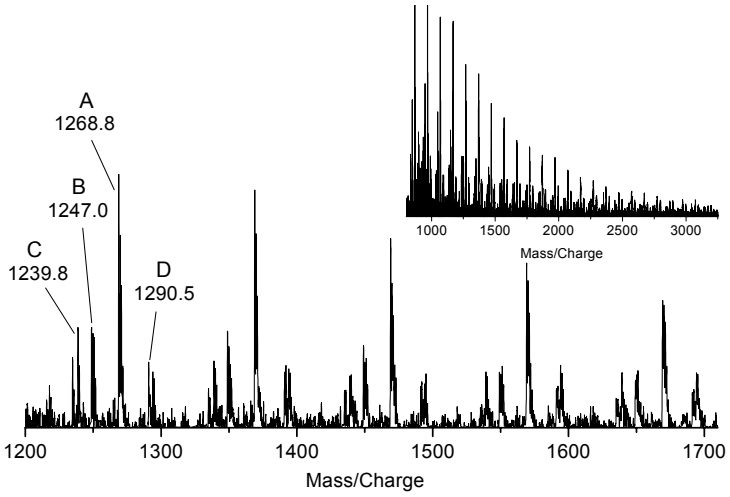


Figure ESI 2. MALDI-ToF-MS spectrum of PSt with a 10:1:1 molar feed ratio of St: ACVA: SEE. Showing the determined chain end groups. Obtained by dried droplet method using dithranol matrix, silver trifluoroacetate salt and THF as the carrier solvent.

C) PMMA produced in presence of **1** at 60˚C (ACVA)

Molar Feed Ratio of MMA/ACVA/SEE	Concentration (mmol/L)			Conv. %	Mn	Mw	PD
	MMA	ACVA	SEE				
10/1/1	1032	103.2	103.2	14	2200	3570	1.6
20/1/1	1032	51.6	51.6	40	3200	6000	1.8
30/1/1	1032	34.4	34.4	46	4300	8400	1.9
30/1 (No SEE)	1032	34.4	-	76	14100	33200	2.4

Table ESI 3 Feed ratios of MMA, ACVA and SEE with the respective molecular weights and conversions obtained



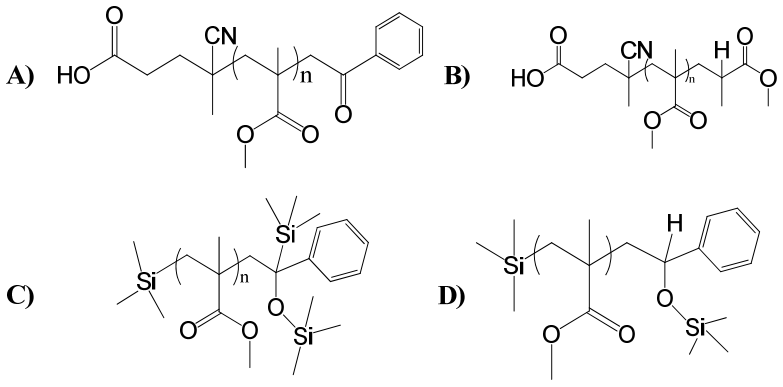


Figure ESI 3. MALDI-ToF-MS spectrum with the determined chain end groups for PMMA with a molar feed ratio of 10:1:1 (MMA: ACVA: SEE). Obtained by dried droplet method using CCA matrix, sodium trifluoroacetate salt and THF as the carrier solvent.

Branched polymers

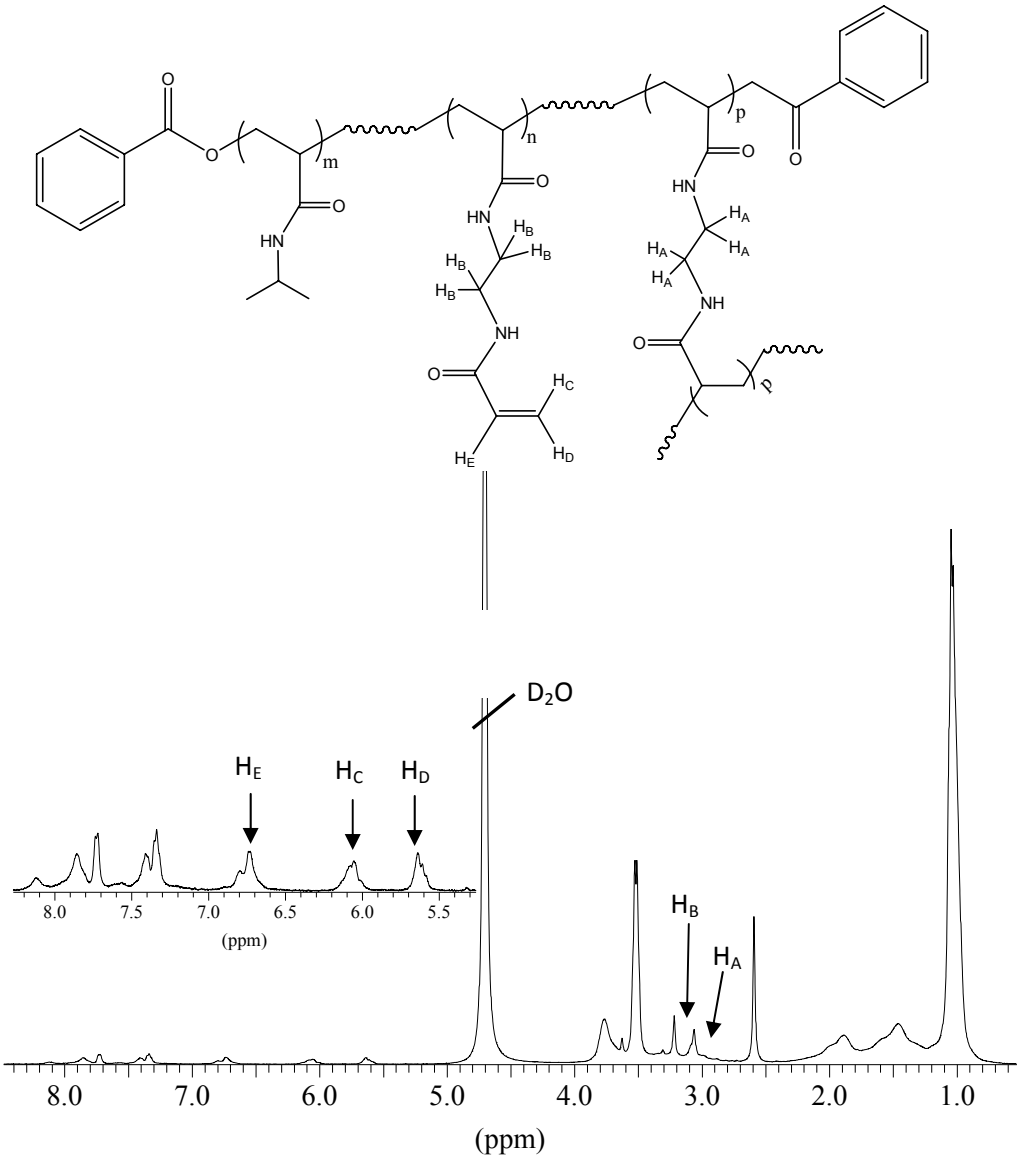


Figure ESI 4. ^{1}H NMR spectrum (D_2O) for P(PNIPAM)-co(EBAAm) with molar feed ratio of 10/1/1/1 (NIPAM/EBAAm/BPO/SEE) with a reaction time of 1 hour.

The degree of branching (branches per repeat unit) for this molecule was calculated to be 0.088 using data from proton NMR and the following equation:

$$DB = N_F/(N_{NIP} + 2\,N_F + N_M)$$

Where N_F is the quantity of fully reacted EBAAm in the polymer, N_M is the quantity of mono reacted EBAAm in the polymer and N_{NIP} is the quantity of NIPAM in the polymer.